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BROWN UNIVERSITY

Technical Report No. 1

I. DIELECTRIC PROPERTIES OF LIQUID ETHANOL AND 2-PROPANOL

By

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II. DIELECTRIC PROPERTIES OF TRIMETHYLENE GLYCOL

By

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November 16, 1953

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ABSTRACT

Dielectric constants and loss were measured from room tempera-
ture to -160°C for the pure liquids and mixtures with small amount.
of water to facilitate supercooling. Two distinct dispersion
regions were found below -100°C in the experimental frequency
range from 1 c/s to 5 Mc/s. The temperature dependences were
similar and described by rate laws of the form found for similar
measurements in 1-propanol. The magnitudes and temperature
dependences of the equilibrium dielectric constants are discussed
in terms of Kirkwood's theory. An explanation of the multiple dis-
persions in terms of hydrogen bond breaking to permit reorienta-
tion of alkyl and hydroxyl groups is discussed.

I. INTRODUCTION

Previously reported work on 1-propanol and related glycols[1]

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1. D. W. Davidson and R. H. Cole, J. Chem. Phys., 19,
   1484 (1951).
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showed that definitive measurements of their dielectric dispersion
and loss were possible in the audio and radio frequency range
by working at sufficiently low temperatures. These measurements
in the case of 1-propanol revealed the existence of three ex-
perimentally distinct dispersion regions[2]

2. R. H. Cole and D. W. Davidson, J. Chem. Phys., 20, 1389 (1952..

all exhibiting the exponential temperature dependence characteristically associated with dielectric relaxation and other rate processes.

In the present work, similar studies were undertaken on the related alcohols, ethanol and 2-propanol, in order to determine the nature of the relaxation spectra and to provide a better basis for interpretation of the observed properties in molecular terms.

The available frequency range of accurate and convenient bridge and transient methods, extending from 1 cycle/sec to 5 megacycles/sec, made adequate measurements possible only in the temperature range of the supercooled liquid below the normal melting point. This necessity presented no great problems in the earlier work on 1-propanol, but was a matter of some difficulty for the present case. It has often been observed that liquids composed of more symmetrical molecules are less readily supercooled, and the alcohols of interest here were no exception.

While a substantial amount of information was obtained for both ethanol and 2-propanol before the onset of freezing, it was not possible from the data obtained to confirm with any great assurance the existence of secondary, higher frequency dispersions previously defined in 1-propanol. However, Tammann and Hesse[3]

3. G. Tammann and W. Hesse, Z. anorg. u. allgem. Chem., 156, 245 (1926).

among others have found that addition of small amounts of water to absolute ethanol facilitated supercooling, even to the extent of glass formation. This effect, found also for 2-propanol,

permitted study of alcohol-rich solutions over a sufficiently wide temperature range.   The properties of the anhydrous alcohols at low temperatures could then be obtained by extrapolation in a manner consistent with the concentration dependence observed at higher temperatures.

By this indirect approach, measurements of dielectric dispersion and loss were made in the range 120-200°K for 2-propanol, and in the range 110-160°K for ethanol.   Equilibrium dielectric constants were determined from the lowest temperature to 300°K in both cases.

II. EXPERIMENTAL METHODS

A. PURIFICATION OF MATERIALS

2-propanol (Eimer and Amend, Tested Purity Reagent) was dried by refluxing over calcium hydride. Upon distillation, the fraction boiling at 82.4°C was collected, and the average room temperature specific conductance for all samples reported was 5.8×10^{-8} $ohm^{-1}cm^{-1}$.

A 13 weight percent mixture of water[*]

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[*]Fractionally condensed conductivity water was provided by E.L.Swarts

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(specific conductance less than $3 \times 10^{-7} ohm^{-1}cm^{-1}$) in 2-propanol was prepared.   The lower boiling fraction (80.4°C; $n_D^{15} = 1.3795$), corresponding to the azeotropic mixture (12.1% water), was collected. A 99 weight percent mixture of 2-propanol in water ($n_D^{15} = 1.3792-3$; 24:1 molecular ratio) was then prepared from the constant boiling mixture and dry 2-propanol.   The average room temperature conductance for all samples reported was $5.4 \times 10^{-8} ohm^{-1}cm^{-1}$.

"Absolute" ethanol was refluxed over calcium hydride, and the fraction distilling at 78.3°C (n_D^{25} = 1.3594) was collected. The average room temperature specific conductance for all samples reported was 8.2 x 10^{-8}ohm^{-1}cm^{-1}.

A 95 weight percent mixture of ethanol in water was distilled, and the lower boiling fraction (78.2°C; n_D^{25} = 1.3611), corresponding to the azeotropic mixture (4.4% water; 8:1 molecular ratio), was collected. The average room temperature conductance for all samples reported was 4.1 x 10^{-7}ohm^{-1}cm^{-1}.

A 99 weight percent mixture of ethanol in water (n_D^{25} = 1.3598; 39:1 molecular ratio) was prepared from the constant boiling mixture and dry ethanol. The average room temperature conductance for all samples reported was 1.1 x 10^{-7}ohm^{-1}cm^{-1}.
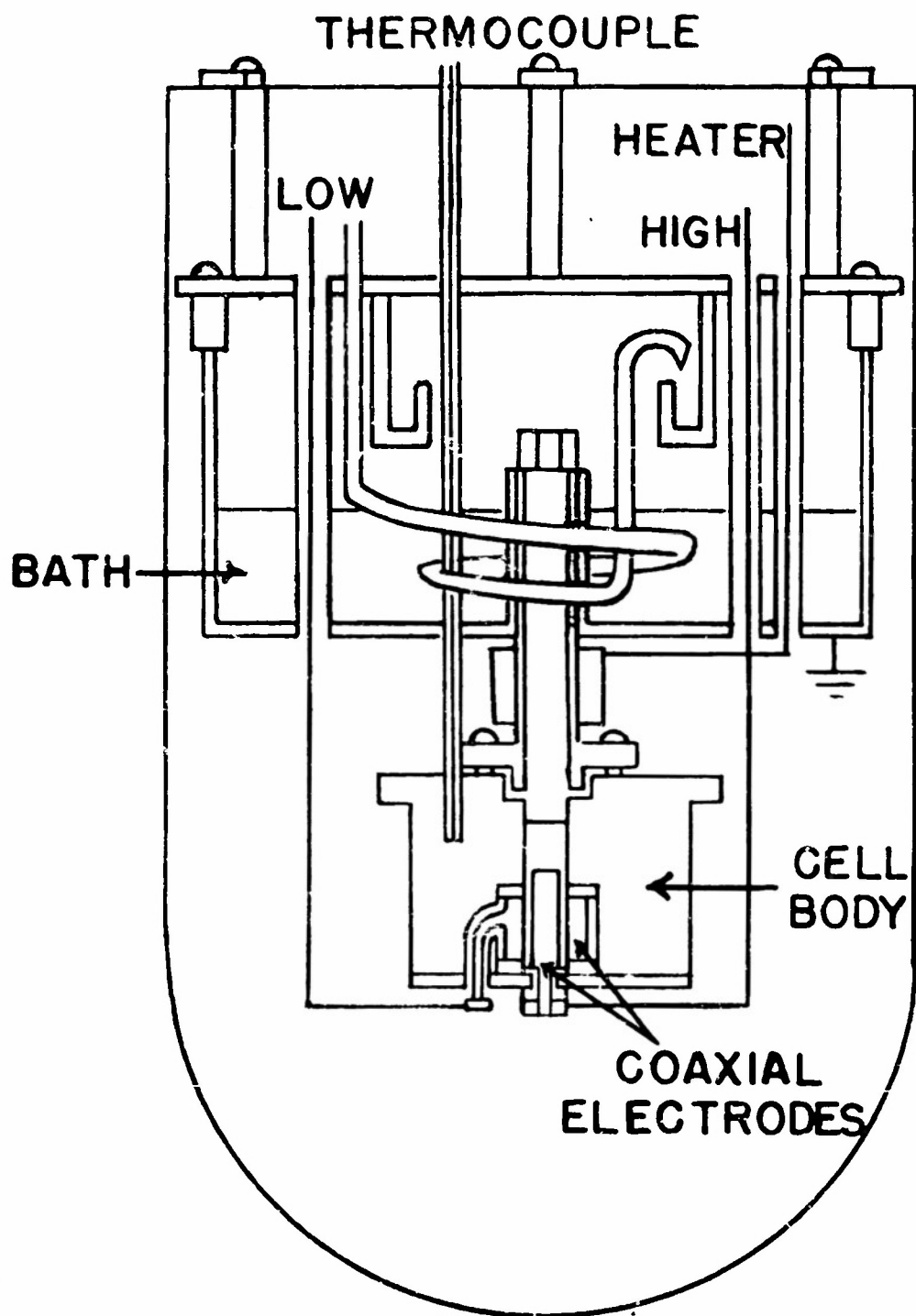
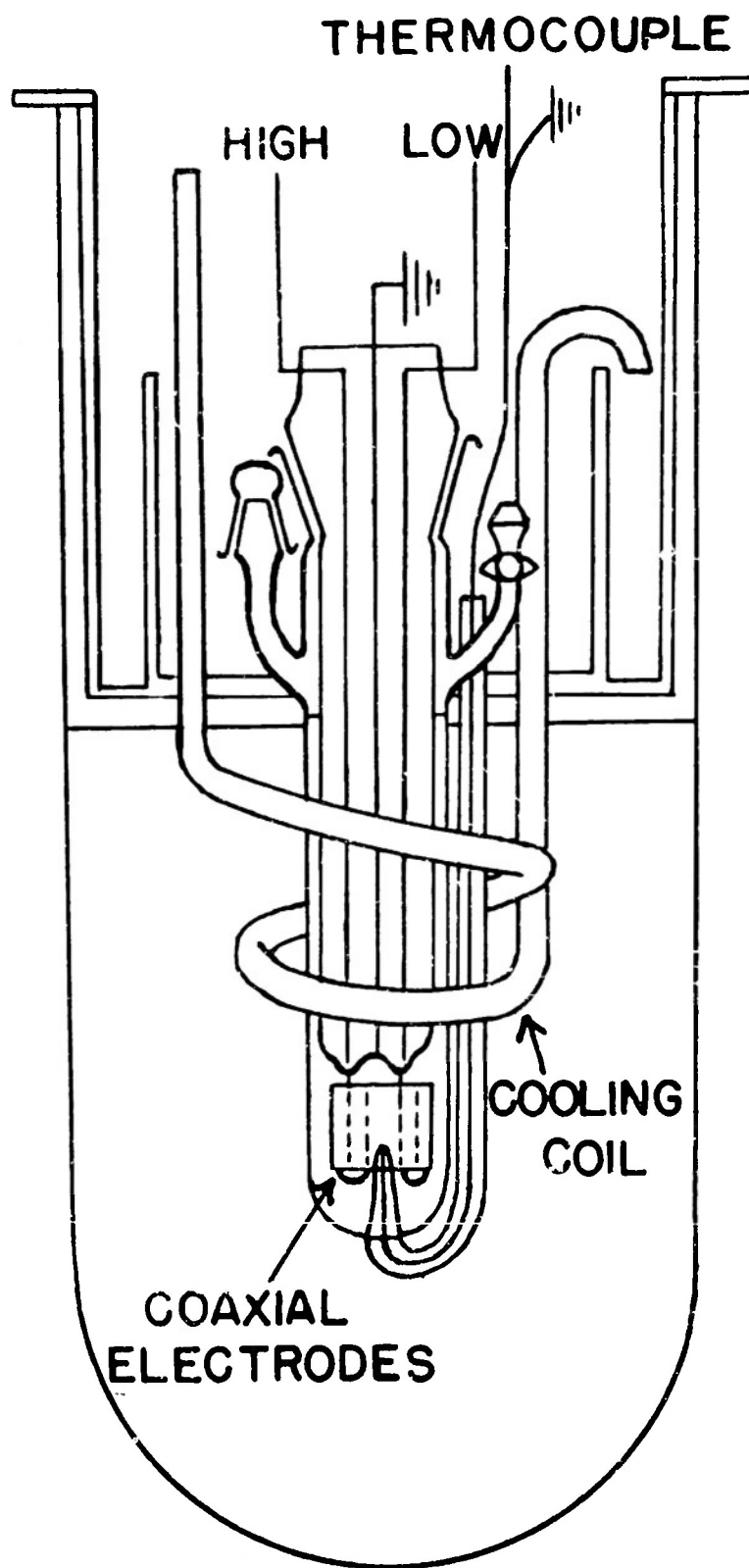B. DIELECTRIC CELLS AND COOLING SYSTEMS

Two cells were employed in the measurements, both embodying coaxial cylindrical electrodes. The first of these was of nickel-plated brass with Teflon insulation and is shown in Fig. 1 in cross section together with the cooling bath and coils and surrounding Dewar flask. The air capacitance was 2.60 $\mu\mu$f, reproducible to one percent on reassembly, and with the electrode dimensions and spacing used required 4 cm^3 of liquid for filling with an ample reserve for contraction on cooling.

The second cell, of nickel and glass construction, from J. C. Balsbaugh of Cambridge, Mass., employed three coaxial nickel cylindrical tubes, the inner and outermost connected together to serve as the low potential electrode, as indicated in the cross section of the cell and associated cooling bath shown in Fig. 2. The lead wires through the glass press had unavoidable direct capacitance, which, however, was kept to a minimum by grounded

Fig. 1.   First cell and cooling arrangement.

Fig. 2.   Second cell and cooling arrangement.

THERMOCOUPLE

HEATER

LOW

HIGH

BATH →

CELL BODY

COAXIAL ELECTRODES

THERMOCOUPLE

HIGH   LOW

COOLING
COIL

COAXIAL
ELECTRODES

shielding of the leads from the press to the bridge. The residual stray capacitance was calibrated by capacitance measurements of a series of six liquids of known dielectric constants from 2 to 80. It was found that these measurements satisfied the equation

$$C(\mu\mu f) = 4.81\epsilon + 1.50,$$

where C is the measured capacitance for a liquid of dielectric constant ϵ. The second cell required a volume of approximately 25 cm^3 for filling with reserve for thermal contraction.

The first cell had the advantage of requiring only a small volume of sample and permitting direct admittance measurements without correction for stray capacitances. The second could be cooled more rapidly, and was useful for measurements of the super-cooled pure alcohols. Comparable measurements were in good agreement. Cooling of both cells to temperatures as low as 120°K was effected by passing liquid nitrogen through cooling coils immersed in a bath liquid devised by Kanolt[4]

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4. C.W.Kanolt, U.S. Bur. Stds. Scientific Paper No. 520, March, 1926.

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to be non-volatile and fluid at low temperature. Temperature control of the first cell was obtained by adjustment of current in a six watt heating coil, and in the second cell by judicious addition of liquid nitrogen to a small annular trough partially immersed in the bath liquid. Ordinarily, constancy to ±0.1° could be realized, but when hurried measurements were necessary to avoid errors from freezing variations of ±0.2° were tolerated.

Copper-constantan couples calibrated at the freezing point of mercury, sublimation point of CO_2, and by comparison with an

oxygen vapor pressure thermometer were employed for temperature measurement, their EMF being read by a Leeds and Northrup Type K potentiometer.

C. ELECTRICAL MEASUREMENTS

The frequency range 15c/s to 5 Mc/s was covered by a bridge described elsewhere[5],

5. R. H. Cole and P. M. Gross, Jr., Rev. Sci. Inst., 20, 252 (1949)

and studies to times of a second or more by a special transient apparatus[6].

6. R. H. Cole, R. P. Auty, and D. W. Davidson, Rev. Sci. Inst., 22, 678 (1951)

With the two methods, a range of seven decades in rate of the dielectric relaxation processes could be studied. Of considerable importance for the success and comprehensive nature of the measurements was the facility and speed with which they could be made once suitable thermal conditions were established; a bridge run at twenty or more frequencies could be completed in forty minutes or less and a transient run required a second or two for the measurement proper (but with the disadvantage of considerable time for reading of records).

III. EXPERIMENTAL DATA

Data were obtained for five different systems in all, at temperatures as summarized in the table below:

Table I. Temperature Ranges of Measurement

Alcohol (Wt.%)	EtOH 100%	EtOH 99%	EtOH 95.6%	2-PrOH 100%	2-PrOH 99%
Temperature Range of Equilibrium Data	130-300°K	110-300°K	117-300°K	178-300°K	123-300°K
Temperature Range of Relaxation Data	130-160°K	110-154°K	117-160°K	178-200°K	123-200°K
Number of Spectra	23	16	14	12	37

Space does not permit even a reasonably complete tabulation of the directly observed quantities. For this reason discussions are first given of the analytical representations found to describe the data, which are followed by tables of the parameters in these equations. (Representative measurements are given in the Ph.D. thesis of F. X. Hassion, Brown University, 1953).

A. EQUILIBRIUM DATA

The equilibrium dielectric constants ϵ_0 were found to be accurately described by the simple equation

$$\epsilon_0 = A + B/T, \qquad (1)$$

where T is temperature in °K. Eq. (1) reproduces the individual measurements of different series, over the ranges indicated by Table I, to within ±1%. The values of A and B for best fit of the data are listed in Table II.

Table II. Constants of the Equilibrium
Dielectric Constant Equation

System	EtOH 100%	EtOH 99%	EtOH 95.6%	2-PrOH 100%	2-PrOH 99%
-A	18.60	21.09	24.20	21.53	23.65
B x 10^3	12.80	13.68	15.26	12.20	12.78

B. LOW FREQUENCY DISPERSION DATA

For all the systems studied, it was found that the first
dispersion encountered with increasing frequency, or at the
longest times in transient studies, was quantitatively described
by the familiar Debye equations characteristic of a simple first
order rate process. These relations in the case of steady state
measurements, as by a conductance-capacitance bridge in the present
work, are conveniently expressed in the complex form

$$\epsilon' - i\epsilon'' = \epsilon_1 + (\epsilon_0 - \epsilon_1)/(1 + i\omega\tau_1). \qquad (2)$$

Here the real and imaginary parts ϵ' and ϵ'', measured as
equivalent parallel capacitance and conductance for frequencies
$F = \omega/2\pi$, are expressed in terms of the limiting dielectric
constants, ϵ_0 and ϵ_1, at low and high frequencies and the
relaxation time τ_1. A more convenient parameter than τ_1 for
many purposes is the corresponding relaxation frequency $f_1 =$
$1/2\pi\tau_1$.

Of the possible ways of testing the validity of Eq. (2) and
determining the parameters ϵ_0, ϵ_1, f_1, we have found most con-
venient first the complex plane loci of ϵ'' versus ϵ', and
second plots of ϵ' versus $f\epsilon''$ and ϵ''/f.

If Eq. (2) represents the experimental results, the locus of
ϵ'' versus ϵ' is a semicircle in the complex plane[7],

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7. K. S. Cole and R. H. Cole, J. Chem. Phys., 9, 341
(1941)

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with intercepts on the real axis (ϵ') at ϵ_0 and ϵ_1. A typical example for each of the systems studied is given in Figs. 3-7. The curves fitting the points are in each case drawn as semicircles, as required by Eq. (2), and represent the data to within their accuracy.

Although such complex plane loci are convenient and sensitive tests of Eq. (2) as a representation of the data, they do not readily give precise values of the relaxation frequency f_1. The frequency dependence predicted by Eq. (2) can be verified, and the value of f_1 determined if the real and imaginary parts of Eq. (2) are written in the form

$$\epsilon' = \epsilon_0 - f\epsilon''/f_1 = \epsilon_1 + f_1\epsilon''/f. \tag{3}$$

Thus plots of measured quantities ϵ' versus $f\epsilon''$ and ϵ''/f should give straight lines of intercepts ϵ_0 and ϵ_1 with slopes $1/f_1$ and f_1, respectively. These procedures, which require no assumption as to values of the parameters ϵ_0, ϵ_1, and f_1, gave straight lines within the accuracy of the data, except at frequencies $f \gg f_1$, and the values listed in Table III were so obtained. Parameters f_2 and ϵ_2 characterizing the higher frequency behavior, which are discussed in C, are also listed in Table III.
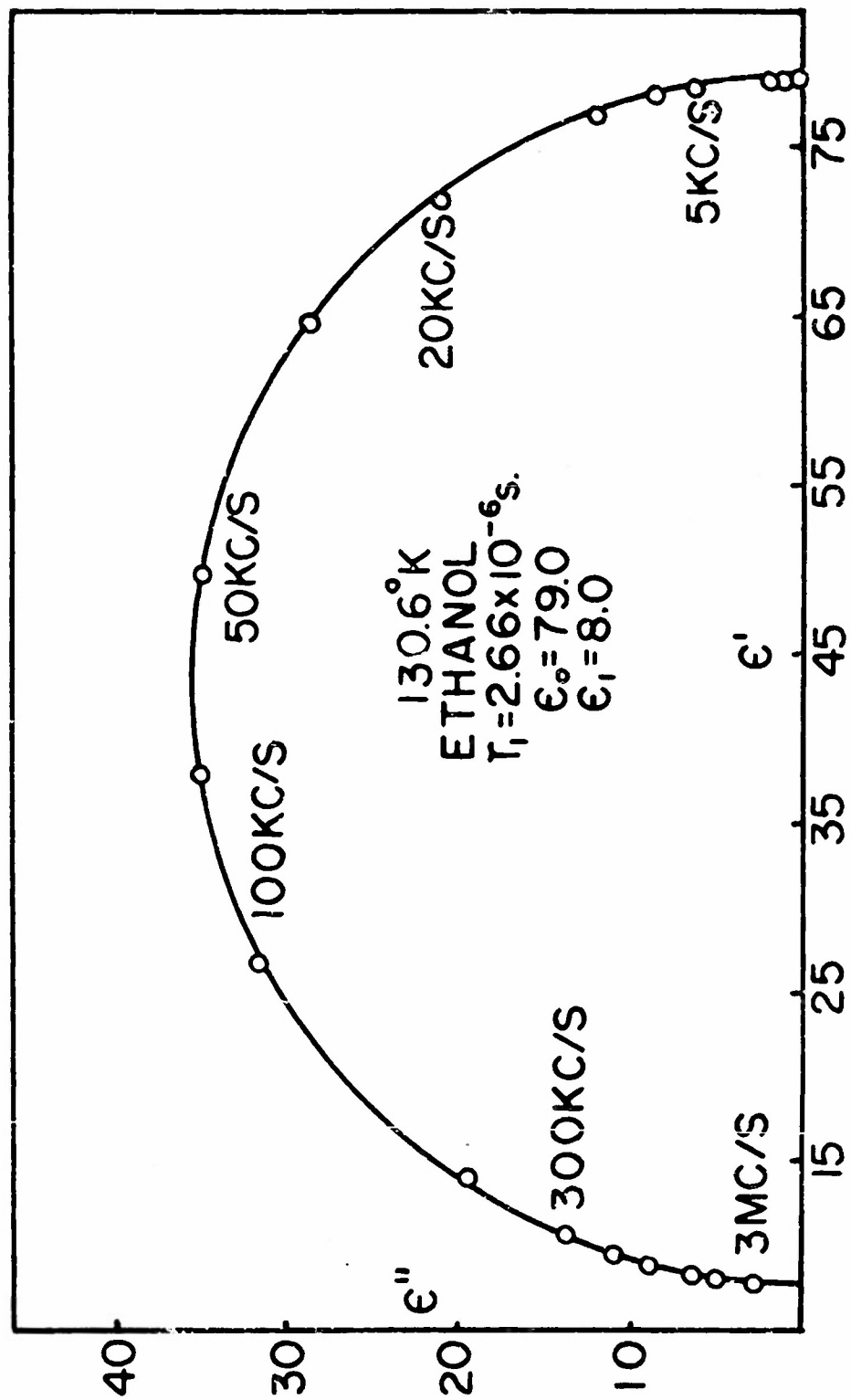
Fig. 3.   Complex dielectric constant of ethanol at 130.6°K.
(In this and following complex loci the numbers
by points indicate frequencies of measurement.)

Fig. 4.   Complex dielectric constant of 99% ethanol at 111°K.
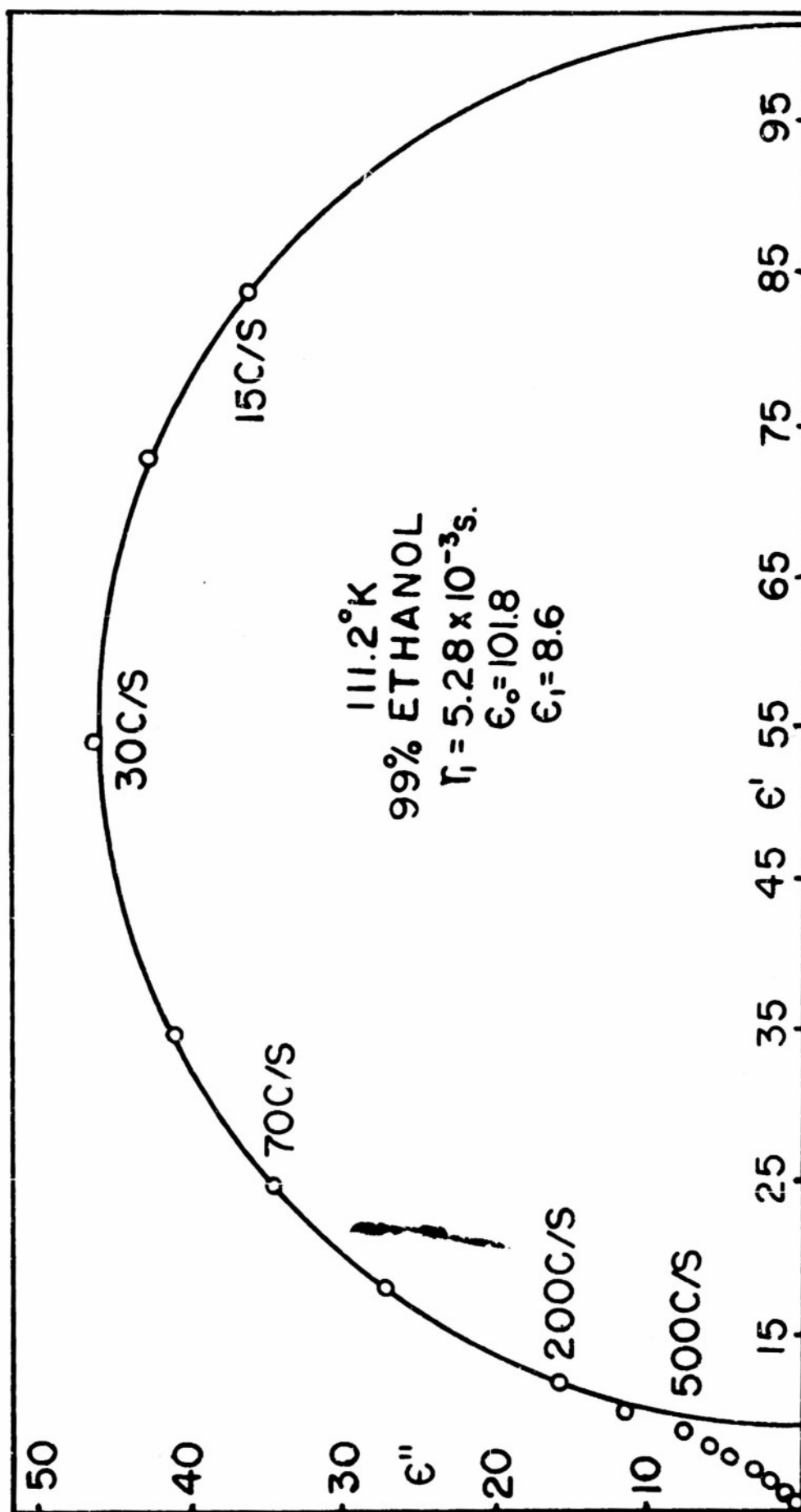
Fig. 5.   Complex dielectric constant of 95.6% ethanol at 128°K.

Fig. 6.   Complex dielectric constant of 2-propanol at 178°K.

Fig. 7.   Complex dielectric constant of 99% 2-propanol at 138°K.

130.6°K
ETHANOL
$T_1 = 2.66 \times 10^{-6}$ s.
$\epsilon_o = 79.0$
$\epsilon_1 = 8.0$

111.2°K
99% ETHANOL
$T_1 = 5.28 \times 10^{-3}$ s.
$\epsilon_o = 101.8$
$\epsilon_1 = 8.6$

95.6% ETHANOL
$T_1 = 4.85 \times 10^{-5}$ secs.
$\epsilon_0 = 94.7$
$\epsilon_1 = 8.6$
128.1° K

177.5°K
ISO-PROPANOL
$T_1 = 1.02 \times 10^{-6}$ secs.
$\epsilon_o = 47.1$
$\epsilon_1 = 4.0$

138.1°K
9.9% ISO-PROPANOL
$\tau_i = 2.75 \times 10^{-3}$ secs.
$\epsilon_o = 67.1$
$\epsilon_i = 5.2$

TABLE III. Parameters of Dispersion in Ethanol and 2-Propanol.
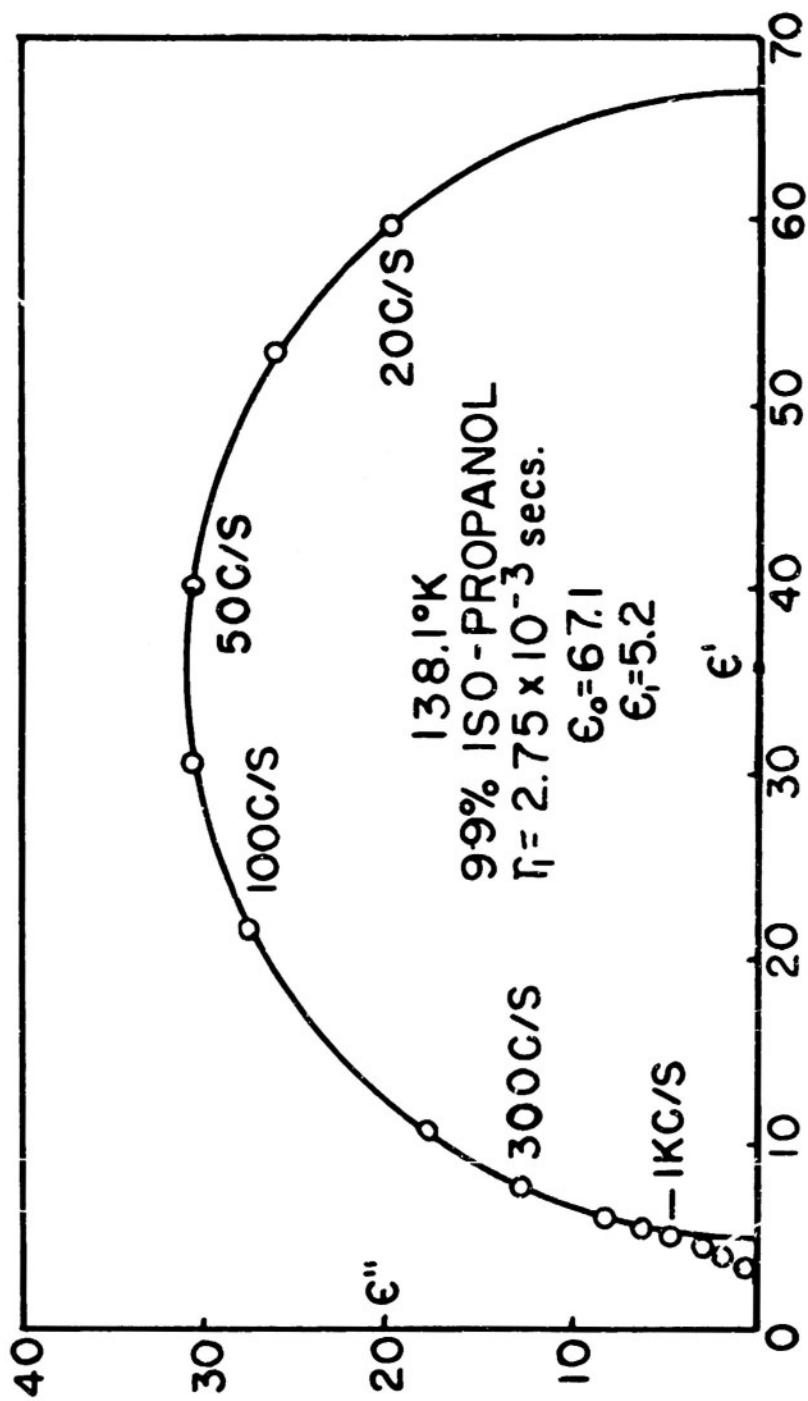(Values in parentheses by considerable extrapolation, data
at starred temperatures by transient measurements.)

A. Ethanol

$T°K$	ϵ_0	ϵ_1	f_1 (kc/s)
159.4	62.6	–	1850
155.6	63.9	(6.0)	1460
148.4	67.3	6.5	755
143.5	71.2	7.2	354
137.3	74.2	7.6	180
133.2	77.2	7.9	95
130.6	79.0	8.0	60

B. 99% Ethanol

$T°K$	ϵ_0	ϵ_1	ϵ_2	f_1 (kc/s)	f_2 (kc/s)
153.7	68.7	–	–	780	–
150.2	71.5	–	–	460	–
138.9	77.8	(7.6)	–	125	–
131.2	84.2	8.1	–	27.7	–
126.0	87.4	8.5	5.1	11.4	1500
120.4	91.7	8.5	4.7	2.67	225
115.3	98.2	8.6	4.7	0.203	14.0
110.1	(102.0)	8.6	4.1	0.0168	0.52

C. 95% Ethanol

$T°K$	ϵ_0	ϵ_1	ϵ_2	f_1 (kc/s)	f_2 (kc/s)
162.3	70.00	–	–	1240	–
153.1	75.4	(7)	–	425	–
145.6	80.9	7.8	–	142	–
141.9	83.7	8.2	–	76	–
133.7	90.1	8.6	(4.9)	14.6	4900
126.0	96.1	9.2	4.7	1.84	460
119.2	101.9	10.6	4.7	0.108	14.0
116.8	(104)	10.6	4.5	0.029	3.1

TABLE III - Continued

D. 2-Propanol

$T^\circ K$	ϵ_0	ϵ_1	f_1 (kc/s)
200.0	39.5	(2.6)	1330
195.3	40.8	3.2	995
190.4	42.7	3.8	603
183.2	44.5	3.9	335
181.1	45.7	4.0	218
177.5	47.1	4.0	156

E. 99% 2-Propanol

$T^\circ K$	ϵ_0	ϵ_1	ϵ_2	f_1 (kc/s)
199.5	40.8	(3.0)	-	1450
189.5	44.2	(3.2)	-	514
179.1	47.5	4.2	-	179
169.5	-	-	-	50.1
138.1	67.1	5.2	3.3	0.058
132.2*	72.7	5.7	2.7	0.0032
128.1*	75.8	5.7	2.8	0.00048
122.9*	80.0	5.9	3.0	0.00002

C. HIGH FREQUENCY DISPERSION DATA

For all five systems studied, the dispersion data give conclusive evidence that a further dispersion exists in addition to the relaxation dispersion described by the parameters ϵ_0, ϵ_1, f_1 of Table III and illustrated in Figs. 3-7. This is evident at all temperatures for which reasonably complete measurements of the first dispersion could be obtained from the fact that the high frequency limiting values of ϵ' are considerably greater than values of order 2.5 to 3 attributable to electronic polarization, these latter corresponding to values of refractive index squared extrapolated to <u>zero frequency.</u>
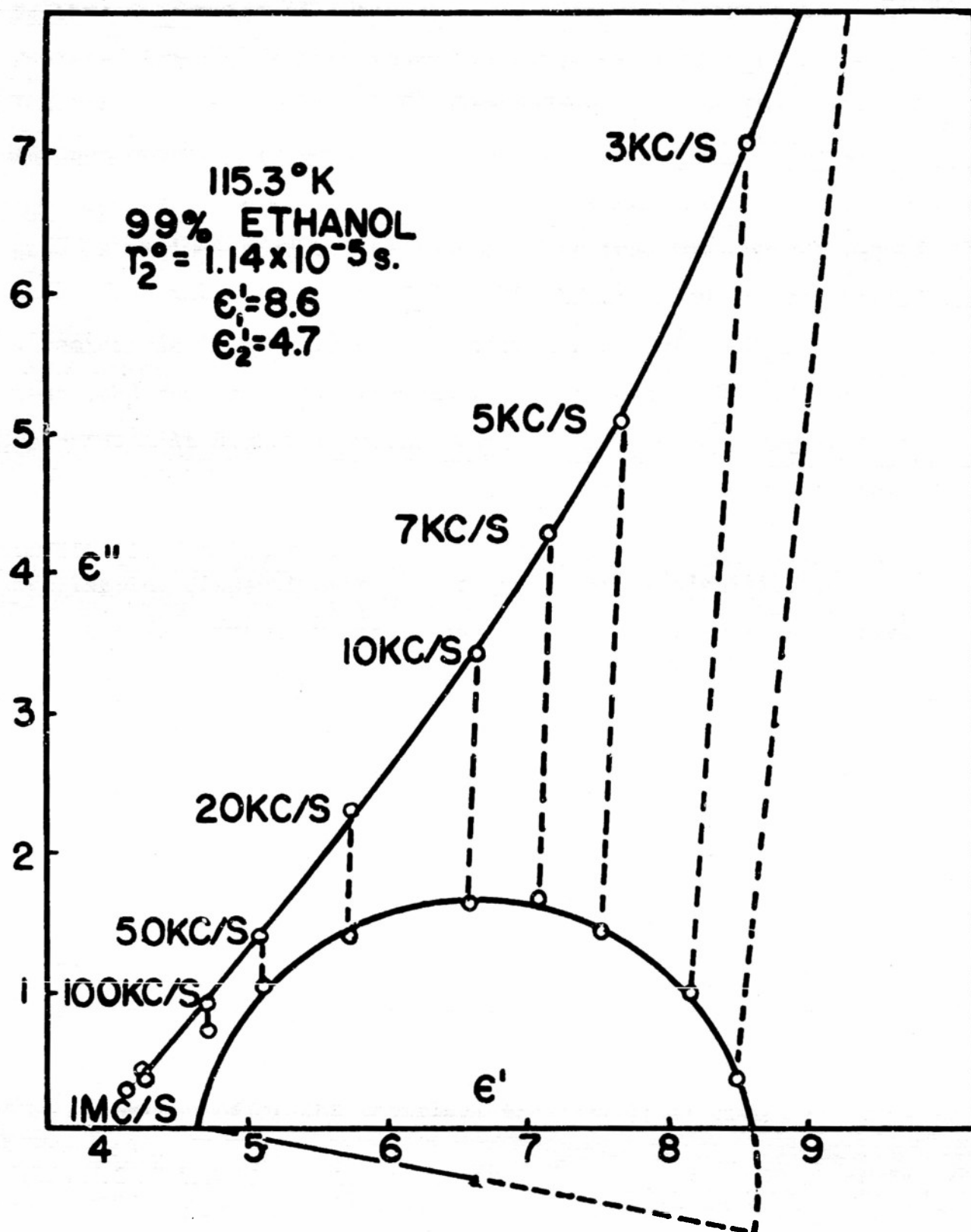
At the lower temperatures, the data make evident that most of the difference is accounted for by further dispersion in the measurement range of audio and radio frequencies. This is illustrated by data for 99 percent ethanol at 115°K, plotted in Fig. 8. In this figure, only the high frequency portion of the complete complex plane locus is shown, in order to make evident the departures from the vertical asymptote at $\epsilon_1 = 8.5$ of the semicircle extending to $\epsilon_0 = 98.2$ which describes data at frequencies below 1 kc/s.

The analytical procedure found to yield a sensible resolution of the similar dispersion in 1-propanol[2] was applied to the present results also. This consists in assuming that the observed complex dielectric constant is a sum of overlapping dispersions, of which the lowest is the Debye dispersion which accounts for most of the dispersion at sufficiently low frequencies:

$$\epsilon^x = \epsilon' - i\epsilon'' = \epsilon_1^x + \epsilon_2^x \tag{4}$$

Fig. 8. High frequency dispersion region in 99% ethanol
at 115°K.

where $\epsilon_1^* = (\epsilon_0 - \epsilon_1)/(1 + if/f_1)$ as before, and ϵ_2^* is the further dispersion of interest here. Since the constants representing ϵ_1^* are known accurately, the necessary real and imaginary parts of ϵ_2^* to fit the data can be obtained from the measured values of ϵ^*.

In the example of Fig. 8, the results of this numerical process are indicated by the dashed lines from the upper locus of ϵ^* to the lower locus of ϵ_2^*. The latter locus is not fitted by a semicircle, but conforms to a circular arc with slightly depressed center until frequencies of the order 100 kc/s are reached. At higher frequencies, the analysis thus suggests still further dispersion but the data are too limited in extent and too sensitive to errors in differences for a further analysis into overlapping dispersions to be of quantitative significance.

All data extending to sufficiently high frequencies showed the behavior illustrated in Fig. 8, except, of course, for scale and range of frequencies. In particular, the secondary dispersions (corresponding to the data between 100 kc/s and 2kc/s in the example) were in all cases fitted reasonably well by a circular arc, but not by a semicircle. The exact depression angle of the radius vector characterizing this form of locus, which has been found to describe many dielectrics[7], is not accurately determinable because of sensitivity of the derived data to small errors, but is of the order 10°-15°. This corresponds to values of 0.11-0.17 for the parameter α of the empirical arc dispersion function:

$$\epsilon_2^* = \epsilon_2 + (\epsilon_1 - \epsilon_2)/\left[1 + (if/f_2)^{1-\alpha}\right] \quad (5)$$

The center frequency f_2 of this arc dispersion can be estimated from the frequency of maximum ϵ'' of the center of the

arc, and the values ϵ_1 and ϵ_2 are the intercepts on the ϵ' axis. These values for the various dispersion measurements from which they could be obtained are listed in Table III.

IV. DISCUSSION

The experimental results presented in Section III give information about two quite distinct but closely related aspects of the dielectric polarization in ethanol and 2-propanol: the equilibrium behavior characterized by the static dielectric constant, and the kinetic behavior represented by the dispersion and absorption measurements. The theory of the former is simpler and better understood and will be discussed first, although certain questions of interpretation are properly considered in the light of the dispersion data.

A. THE EQUILIBRIUM DIELECTRIC CONSTANT

The increase of static dielectric constant ϵ_0 with decreasing temperature is well known to be characteristic of polar liquids, and the relatively large values found for the alcohols have long been attributed to association as a result of intermolecular hydrogen bonding. The first adequate formulation of equilibrium theory for dipole polarization in liquids in which account can be taken of such short range correlation between a molecule and its neighbors is due to Kirkwood[8].

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8. J. G. Kirkwood, J. Chem. Phys., _7_, 911 (1939).

Kirkwood's equation can be written

$$\epsilon_0 - \epsilon_\infty = 4\pi \left[\frac{3\epsilon_0}{2\epsilon_0 + 1} g \mu^2 \right] \frac{N}{3kTV} , \qquad (6)$$

where ϵ_∞ is the dielectric constant for induced polarization, $\underline{N}$ is Avogadro's number, $\underline{V}$ the molar volume and **kT** has the usual significance. The quantity μ represents the dipole moment of a molecule, considered as the sum of its permanent moment μ_0 as measured in the gas phase and its average induced moment from intermolecular fields in the liquid. The quantity $g\mu$ represents the average moment of an infinite body of the medium for a particular orientation of the single molecule of moment μ.
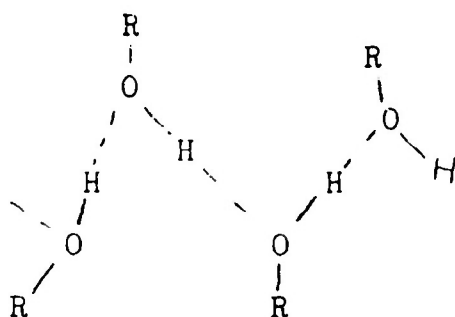
The correlation factor for alcohols has been estimated by Oster and Kirkwood[9]

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9. G. Oster and J. G. Kirkwood, J. Chem. Phys., <u>11</u>, 175 (1943).

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from a model of hydrogen bonding as extended linear chains of the form

By neglecting interchain interactions and assuming free rotation about OH - - O bonds, the factor g is shown to be

$$g = 1 + 2\,\frac{(\mu_H + \mu_R)(\mu_H + \mu_R \cos\varphi)}{\mu_0^2}\cot^2\frac{\varphi}{2}, \tag{7}$$

$$\mu_0^2 = \mu_H^2 + \mu_R^2 + 2\mu_H\mu_R \cos\varphi, \tag{8}$$

where μ_H is the OH bond moment, μ_R the OR group moment, μ_o is the moment of the isolated molecule, and φ the bond angle, which is also taken to be twice the angle between the C-O bond and the plane of hydrogen bonding.

The relation between μ and μ_o is not easily calculated accurately, but Onsager's continuum model leads to the approximate expression

$$\mu = \left(\frac{\epsilon_\infty + 2}{3}\right)\left(\frac{2\epsilon_0 + 1}{2\epsilon_0 + \epsilon_\infty}\right)\mu_o . \qquad (9)$$

With these results, Kirkwood's Eq. (6) becomes

$$\epsilon_0 - \epsilon_\infty = \left(\frac{3\epsilon_0}{2\epsilon_0 + 1}\right)\left(\frac{\epsilon_\infty + 2}{3}\right)^2 \frac{4\pi N g \mu_o^2}{9kTV} , \qquad (10)$$

where g is given by Eq. (7). If the values μ_o = 1.68 debye, μ_H = 1.50 debye, μ_R = 1.2 debye, φ = 105° are used, g has the value 2.39 (Oster and Kirkwood gave g = 2.57 with μ_R = 0.7 debye, a value which is not consistent with Eq. (8) for μ_o. The value 1.2 debye corresponds to C-O and C-H bond moments of 0.8 and 0.4 debye as usually given).

Comparison of Eq. (10) with experiment meets with the difficulty of assigning a proper value to the dielectric constant ϵ_∞ for induced polarization. Possible choices for which arguments can be advanced are the following:

a) ϵ_∞ is the extrapolated square of refractive index of the liquid determined at visible frequencies.

b) ϵ_∞ is the short wave length limit of far infrared (50-150 μ) dispersion results.

c) ϵ_∞ is the high frequency limit of the dispersions at audio and radio frequencies observed in the present work.

Because the quantity (ϵ_∞ + 2) appears as a square in Eq. (10), the predicted values are sensitive to the choice made. Before

considering the arguments for these, the predictions corresponding
to each are expressed by the values of g required to give agreement
of calculated and experimental values of ϵ_r ; these values are
thus to be compared with the value g = 2.39 predicted by the model.
These results are listed in Table IV together with the corresponding
values of ϵ_∞ for the choices a, b, c above.

TABLE IV.   Calculated Correlation Factors to Give
Agreement with Measured Dielectric Constants

a) ϵ_∞ from refractive indices (calculated from n^2 at room
temperature by the Clausius-Mossotti formula)

	Ethanol				2-Propanol			
t°C	22.0,	-8.1,	-49.3,	-101.1	21.5	0 ,	-49.1,	-101.8
ϵ_∞	1.80	1.83	1.88	1.94	1.84	1.87	1.93	1.99
g	3.32	3.41	3.55	3.66	3.33	3.51	3.82	4.11

b) ϵ_∞ from infrared dispersion $n^2 = 2.2$ at 50μ and room
temperature.

ϵ_∞	2.20	2.25	2.33	2.44	2.20	2.24	2.33	2.43
g	2.68	2.75	2.83	2.86	2.77	2.89	3.12	3.32

c) ϵ_∞ from high frequency limit of measured dispersion of ϵ'.

ϵ_∞	2.95	3.05	3.21	3.42	2.44	2.50	2.61	2.74
g	1.90	1.91	1.93	1.90	2.44	2.55	2.74	2.89

For any of the alternative choices of ϵ_∞ it is evident
that the values of g to secure agreement with experiment increase
at lower temperatures and, except for those computed from the
limiting radio frequency value of ϵ' in the case of ethanol, are
appreciably larger than the value 2.39 for the linear chain model.
This temperature dependence is what would be expected for
increased bending or breaking of bonds at higher temperatures, and

the indications of a limiting value at sufficiently low temperatures would then correspond to complete chainwise association by rigid bonds.

Of the three classes of ϵ_∞ , it seems certain that the value $\epsilon_\infty = n^2$ for visible light, and hence essentially electronic polarization, is too small, as some contributions of induced polarization by nuclear displacement must exist. The difficulty is in making any estimate of this further contribution to ϵ_∞ . The values 2.2 to 2.4 correspond to frequencies in the infrared with energy differences of order kT (for $\lambda = 50\mu$, $\overline{\nu} = 200$ cm^{-1} and kT/hc $= 140$ cm^{-1} at 200°K). This suggests that the increases at lower frequencies are more nearly characterized as $\cdots$ polarizations associated with reorientation of classical permanent moments to reach equilibrium with the field and thermal fluctuations. The appropriate values of g for the short range correlation would therefore most reasonably be taken as lying in the range 2.7 to 3.3. These are definitely larger than g = 2.4 of the free-rotation chainwise association model, but the discrepancy is hardly surprising in view of the various approximations in making the comparison.

A more detailed examination of the relation of experimental results to the present approximate theory seems unwarranted. It should perhaps be emphasized that the empirical expression $\epsilon_0 = A + B/T$, with values of A and B to fit the data as given in Table II, has only a superficial resemblance to Eq. (10) of the Kirkwood theory and simplified model of short range correlation of molecular orientations. This is evident from the large negative values of A fitting the data. At higher temperatures, the functional dependence must be different in order to preserve

the necessary condition that $\epsilon_0 > 1$. Comparison of the slope B of this equation with some suitably arranged coefficient of 1/T in Eq. (10) is thus not justified.

From this discussion, it appears that significant correlation of orientations of neighboring molecules occurs at all temperatures of the measurements, that this correlation becomes better established at low temperatures, and that cal ulations from the approximate models are qualitatively but not quantitatively in agreement with the observed equilibrium dielectric constants.

B. TEMPERATURE DEPENDENCES OF THE DISPERSIONS

Both the primary and secondary dispersions exhibit characteristic frequencies depending strongly on temperature in the manner characteristic of relaxation or rate processes controlled by available thermal energy. The relaxation frequencies f_c have the character of specific rate constants for approach to thermal equilibrium, and the normal plots of log f_c versus reciprocal absolute temperature are indicated for analysis of the data. These plots in Fig. 9 show that a linear plot is <u>not</u> obtained for the considerable range in 1/T of the solution measurements, nor can it be said that data for the anhydrous alcohols would if extended conform to such a solution.

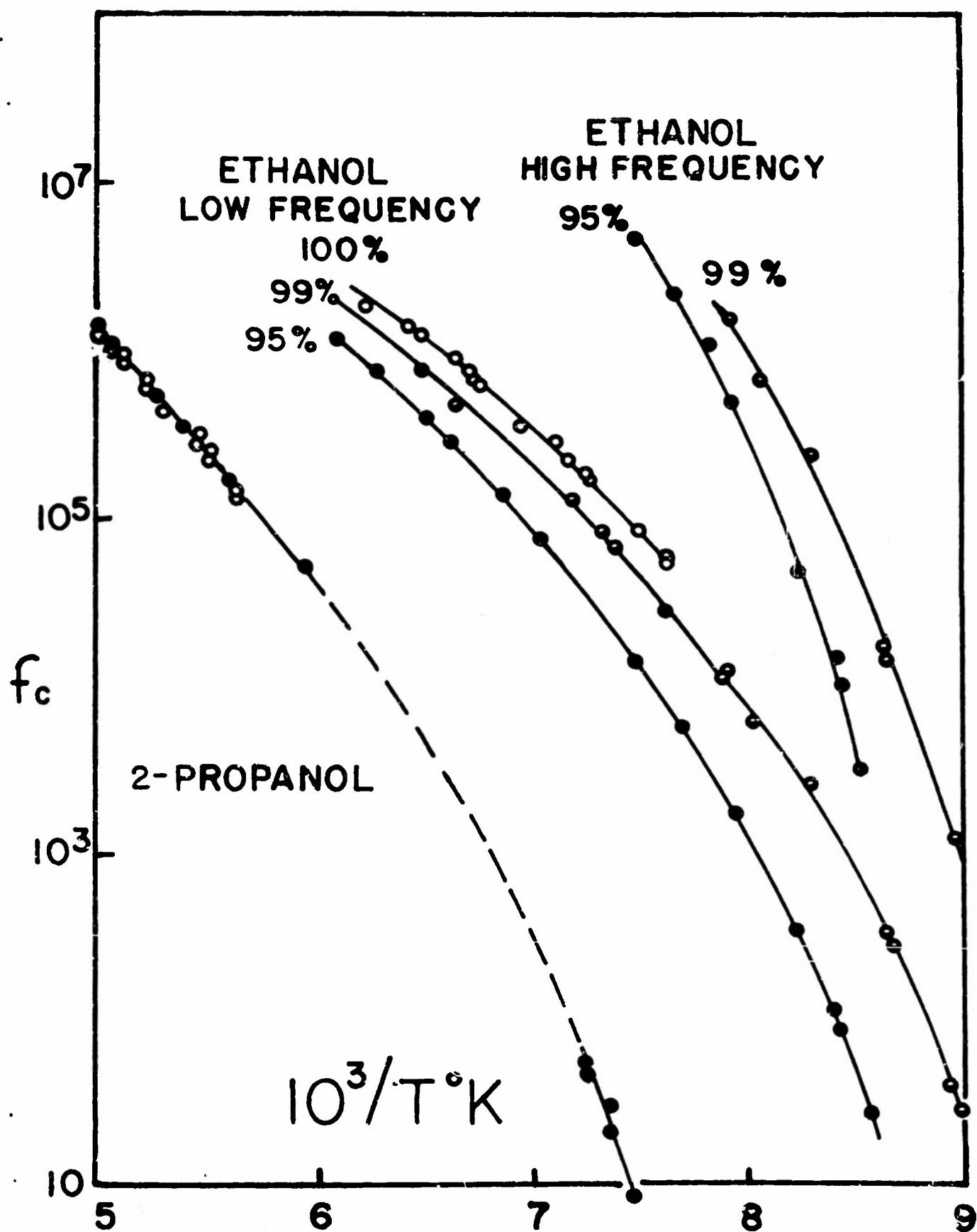The solution data can be fitted by an empirical expression

$$\log f_c = A - B/R(T - T_\infty) \tag{11}$$

for suitable choice of T_∞, as shown in Fig. 10. By analogy with this agreement and the similar results for 1-propanol[1], expressions of the same form were fitted to the more limited data for the pure alcohols, and the necessary parameters A, B, for the values of T_∞ best fitting the solution data are given in Table V.

Fig. 9. Rate plots of log relaxation frequency against
reciprocal absolute temperature.

Fig. 10. Plots of log relaxation frequency against reciprocal
of $T-T_\infty$ (T is temperature in degrees K, T_∞ is an
empirical constant equal to 80°K for ethanol and
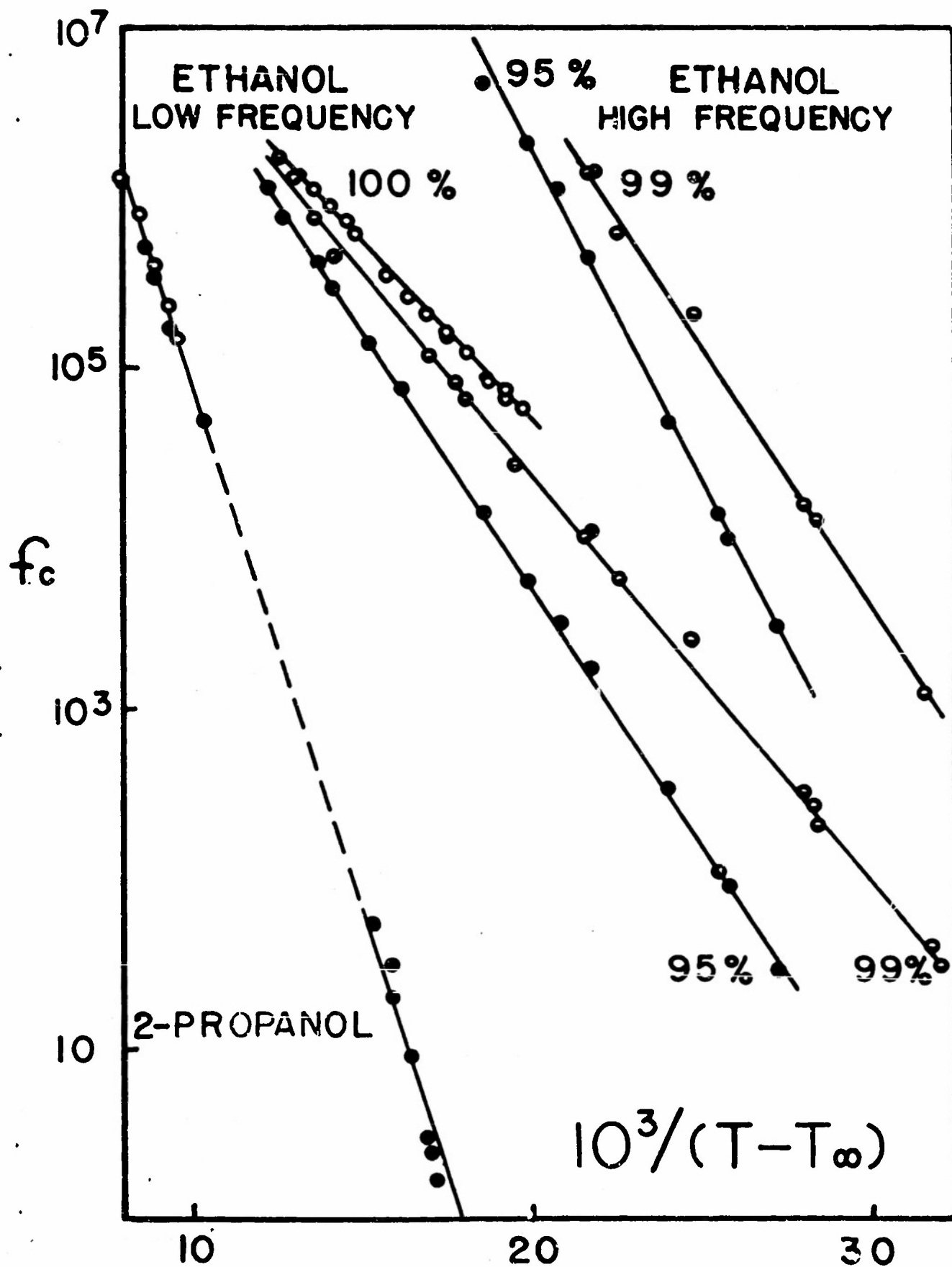73°K for 2-propanol.)

TABLE V.   Rate Law Parameters for Dispersions in Ethanol
and 2-Propanol.
(Values given are for common logarithms to base
10 as in Eq. (11)).

A. Low Frequency Dispersion

System	A	B	$T\infty$	Range of T($^\circ$K)
Ethanol	9.00	215	80	130-159
99% Ethanol	9.06	235	80	110-154
95% Ethanol	9.90	308	80	116-162
2-Propanol	10.43	546	73	177-200
95% 2-Propanol	10.92	604	73	134-200

B. High Frequency Dispersion

System	A	B	$T\infty$	Range of T($^\circ$K)
Ethanol*	(12.44)	(270)	(80)	116-126
99% Ethanol	12.74	303	80	110-126
95% Ethanol	13.32	400	80	116-133

*Values are estimated by extrapolation.

The following conclusions can be drawn from the results.
For both alcohols:

1).   The lower frequency dispersion is accurately described
by Debye equations with single relaxation times, and the higher
frequency dispersions are a little broader,

2).   Both dispersions change even more sharply with tempera-
ture than is predicted by the exponential dependence characteristic
of rate processes,

3).   The familiar concept of an activation energy for ap-
proach to equilibrium is consistent with the data only if the
energy barrier is strongly temperature-dependent with a correspond-
ingly temperature-dependent activation entropy,

4).   The temperature dependences of the rates for the two
dispersions are very similar, as the ratios of critical frequencies

change only by small factors when the frequencies change
separately by several powers of ten.

C. ORIGINS OF THE DISPERSIONS

The very similar temperature dependence of the two dispersions
and the similarity of the earlier results for n-propanol are
striking features for which an adequate theory must account. The
most reasonable explanation we can propose has been outlined in a
recent note[10]

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10. F. X. Hassion and R. H. Cole, Nature, 172, 212 (1953).
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and is discussed in more detail here. It derives
from the linear short range coordination of hydrogen bond moments
found in x-ray studies of liquid[11] and solid alcohols[12]

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11. G. G. Harvey, J. Chem. Phys., 7, 878 (1939).
12. K. J. Tauer and W. N. Lipscomb, Acta Cryst., 5,
    606 (1952).
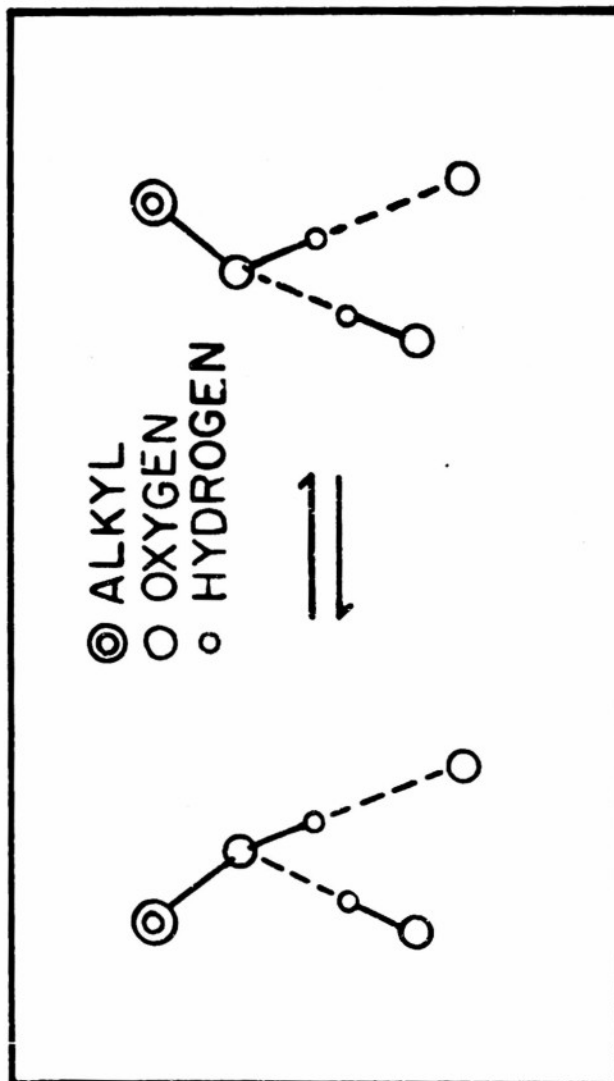---

which
Kirkwood and Oster[9] took as a basis for their equilibrium calcula-
tions. For any particular local bonding of a given molecule with
two neighbors, two configurations of the alkyl group with the
plane of the hydrogen bonds are possible, as shown in Fig. 11.
When an electric field is applied, the orientation for which the
alkyl group moment makes a smaller angle with the field is of
lower energy. The rate of reorientation to permit this equilibrium
configuration will depend on the frequency with which cooperation
of neighboring molecules makes the better sites available, and
on the energy barrier for the accompanying shift of the hydrogen
bond.

It is reasonable to suppose that reorientation of hydroxyl

Fig. 11. Configuration of bonded neighboring alcohol
molecules.

ALKYL
OXYGEN
HYDROGEN

groups is accomplished by breaking of bonds and forming new bonds to other neighbors. This process is also governed by hydrogen bond energy but requires in addition a favorable configuration of a neighbor available for rebonding. As a result, the proposed relaxation process for alkyl groups would be expected to be faster than the relaxation of hydroxyl moments, essentially as a matter of entropy and with similar cooperative energies of activation for the necessary molecular rearrangements.

The fact that the low frequency dispersion is accurately fitted by equations derived from a single relaxation process is consistent with breaking of bonds as the rate determining step, while a model based on reorientation of segments in longer lived bonded chains would result in a distribution of relaxation times for various degrees of chain twisting.

It is therefore proposed that the smaller high frequency dispersions result from reorientation of alkyl group moments, μ_{OR}, while the larger dispersion at lower frequencies results from the net reorientation of hydroxyl group moments, μ_{OH}, by changes in hydrogen bonding. The higher frequency contributions from alkyl groups for random arrangements of hydroxyl bonded groups should be much the smaller for three reasons:

a). The group moment μ_{OR} is smaller (1.2 debye versus 1.5 debye for μ_{OH}),

b). The net moment for possible reorientations of μ_{OR} is small, as only the component of μ_{OR} normal to the plane of hydrogen bonding in Fig. 11 changes,

c). The correlation of neighboring dipoles with a given μ_{OR} does not lead to a significantly enhanced effective moment.

A rough estimate of the relative dipole contributions can

be made as follows. The change in the moment μ_{OR} is that of the component $\mu_{OR} \sin \frac{\varphi}{2}$, where φ is the angle between the two possible positions. The average moment parallel to an effective local field E_{OR} if the OH moment is randomly oriented is found from a simple modification of the familiar Debye treatment to be

$$\overline{\mu_{OR} \cdot E_{OR}} = \left(\mu_{OR} \sin \frac{\varphi}{2} \right)^2 \frac{E_{OR}}{3kT} .$$

The corresponding contribution of μ_{OH} on this crude basis is

$$\overline{\mu_{OH} \cdot E_{OH}} = \left(\mu_{OH} \right)^2 \frac{E_{OH}}{3kT}$$

and the ratio r of the two polarizations is

$$r = \left(\frac{\mu_{OR} \sin \frac{\varphi}{2}}{\mu_{OH}} \right)^2 \frac{E_{OR}}{E_{OH}} .$$

The effective fields E_{OR} and E_{OH} should be obtained from a proper statistical treatment, but for the present development, we may estimate that E_{OH} will because of correlation by hydrogen bonding be larger than E_{OR} by roughly the Kirkwood correlation factor g = 2.5-3. For $\varphi = 105°$, $\mu_{OR} = 1.2$, $\mu_{OH} = 1.5$, this gives r = 0.12-0.15.

This figure is in only qualitative agreement with the observed ratio of extents of the two dispersions, which is about 0.05, but suggests that a more realistic calculation would account for the observed polarizations more quantitatively.

The proposed explanation receives its strongest support, however, from the comparison of the two dispersions in the alcohols so far studied. The interpretation in terms of hydrogen bond breaking and reforming to permit reorientation of the alkyl and hydroxyl groups gives a straightforward and consistent basis for understanding the following facts:

a). The two dispersions have the strong temperature dependence characteristic of relaxation processes,

b). The temperature dependences are similar over a wide range, which indicates similar energy requirements,

c). The higher frequency dispersions are of much smaller amplitude,

d). The dispersions for ethanol, 1-propanol, and 2-propanol are strikingly similar, indicating that a common explanation of their origins should be possible for all three,

e). The low frequency dispersion has simple Debye characters, and the others do not differ drastically from it.

Measurements in progress for methanol and 1-butanol indicate similar behavior in these alcohols also. A comparison of differences in detail of the rate laws for the dispersions and discussion of their implications will be more fruitful when more complete data are available from these measurements, and will therefore be presented later.

The objection might be raised that the reorientation of alkyl groups for fixed hydroxyl configurations of hydroxyl groups is rather like the dog wagging when its tail is fixed. However, the same net result can come about by combinations of torsions of the hydrogen bonded chains which produce no net reorientation of hydroxyl groups with reorientations of the C-O bond without rigid displacement of the entire alkyl group.

D. COMPARISON WITH OTHER RESULTS

The present findings are relevant to a number of results under different conditions for the same and other alcohols which have been reported and discussed by other workers.

The most directly related results of this kind are from

Saxton and Lane's microwave frequencies[13].

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13. J. A. Saxton and J. A. Lane, Proc. Roy. Soc. Lond.,
    213A, 473 (1952)

For ethanol the principal dispersion was taken to have a central wavelength (in vacuum) of 27 cm at 20°C, and the limiting high frequency dielectric constant ϵ_1 of this dispersion was estimated to be 4.4. Further dispersion was found at millimeter wavelengths centered at about 1.3 cm, which was estimated to reduce the dielectric constant to about 2.2. In a second paper, Saxton[14]

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14. J. A. Saxton, Proc. Roy. Soc. Lond., 213A, 473 (1952).

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attributed this second dispersion to a damped resonance process of unspecified molecular origin, but it is more reasonable to consider it as the counterpart of the secondary relaxation dispersion observed at lower temperatures and frequencies in the present work, and hence to attribute it to the relaxation process just discussed. Saxton and Lane have also measured methanol and found a second dispersion region at about 2.5 mm wavelength of which a similar interpretation can be given.

Magat, Dalbert, and Surdut[15]

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15. M. Magat, R. Dalbert, and A. Surdut, Bull. Soc.
    Chim. France, 16, D345 (1949).

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have reviewed earlier, less accurate, measurements for various alcohols, but were unable to come to firm conclusions because of the considerable scatter. They did, however, discuss the possibility of librations (damped torsional

oscillations) of molecules in the fields of neighbors as an
explanation of possible dispersions at millimeter wavelengths or
less at room temperature. Unfortunately, there are no unambiguous
results for the temperature dependence of such dispersions near
room temperature, and nothing can be said with any confidence on
this question.

Recently Mme. Dalbert[16]

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16. R. Dalbert, J. de Chim. Phys., 50, 329 (1953).

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has reported results for 1-octanol
and 2-octanol at several temperatures above -30°C which show that
the high frequency limit of the principal dispersion is significant-
ly larger than n^2, and that the further dispersion must be at
frequencies considerably above 40 Mc/s. She advanced some form
of resonance dispersion as the most likely possibility, but it
again seems reasonable that the relaxation process advanced here
is the proper explanation for much of the difference.

Finally, it should be mentioned that a similar discrepancy
exists in the case of water. A region of increase of ϵ from 2
to about 4.5-4.9 was found centered about a wavelength of 70μ at
20°C by Cartwright and Errera[17].

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17. C. H. Cartwright and J. Errera, Proc. Roy. Soc.
Lond., 154A, 139 (1936).

The hydrogen bonding in water
is, of course, quite different than in alcohols, and the explana-
tion for the latter could not apply to water. It does seem
important for an understanding of the dielectric behavior of water
that more complete studies of the dispersions, especially as

functions of temperature, be undertaken when techniques are developed for the experimentally difficult frequency regions of interest.

DIELECTRIC PROPERTIES OF TRIMETHYLENE GLYCOL

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This work was supported by ONR .

ABSTRACT

Results of dielectric constant and loss measurements to
-70°C at frequencies below 5 Mc/s are discussed. The complex
dielectric constant is not represented by a Debye function, but
can be fitted by an empirical dispersion function of the same form
describing measurements for glycerol and propylene glycol. The
measured properties are intermediate between those for the latter
two, and are compared with them.

I. INTRODUCTION

The properties of trimethylene glycol, $CH_2OHCH_2CH_2OH$
(1-3 propanediol), are of interest in comparison with those of
other three carbon polyhydric alcohols which have been determined
and reported elsewhere[**].

[**]For measurements of glycerol, propylene glycol, and
n-propanol, see Reference 1, for iso-propanol, see
Part 1 of this report.

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1. D. W. Davidson and R. H. Cole, J. Chem. Phys., 19,
   1484 (1952).

Exploratory measurements were made
some time ago by Mr. D. W. Davidson in this laboratory. Con-
siderable difficulties were encountered with sample purity and in
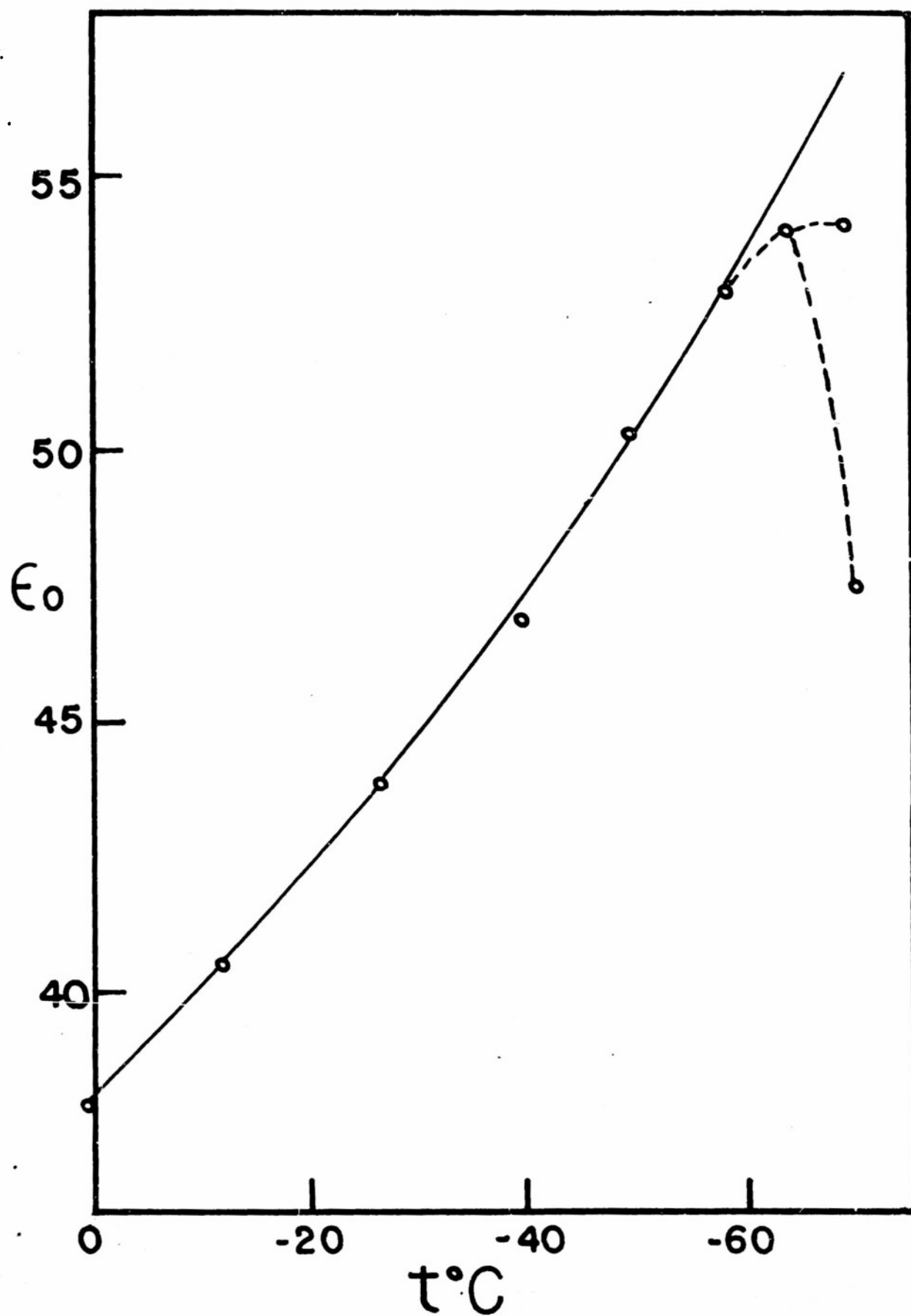supercooling the liquid sufficiently to obtain dispersion

measurements in the available frequency range. At that time, it seemed better to concentrate attention on other systems rather than continue the work with prospects of only limited further accomplishments. Enough data were obtained, however, to give significant information about the temperature dependence of the dielectric constant and the nature of the dispersion process. The results of analysis of these data are presented here.

II. EXPERIMENTAL

Samples of trimethylene glycol as received from Matheson and from Eastman Kodak (practical grade) were distilled under reduced pressure (5 mm) and middle fractions taken. The specific conductances were rather high (ca 10^{-5} mho/cm at room temperature) and were not greatly improved by drying with Mg ribbons or Na_2SO_4 and redistillation. Measurements of dielectric constant and loss at lower temperatures gave quite consistent values as discussed below and this agreement gives reason for confidence that the results obtained are moderately accurate.

The experimental procedure and apparatus were essentially as previously described[1]. Supercooling below the freezing point at ca-30°C proved a matter of considerable difficulty, but in one run it was possible to reach -70°C without appreciable solid formation. This conclusion was reached on the basis of the observed variations of equilibrium dielectric constant with temperature. As with other strongly polar liquids, one expects a smooth increase of dielectric constant ϵ_0 with temperature and much smaller, nearly constant values for the solid. The occurrence of freezing should then manifest itself as departures from a smooth plot of ϵ_0 versus temperature, and just this behavior was found, as shown in Fig. 1. On two occasions when

Fig. 1.   Static dielectric constant ϵ_0 of trimethylene
          glycol at various temperatures.   Dashed curves
          show decreased values as a result of freezing.

freezing was indicated by this comparison of data, the cell was rapidly dismantled and found to contain considerable quantities of white suspended solid globules.

With the above criterion as a guide, only data exhibitng consistent and high dielectric constants were further analyzed to obtain the results reported below. It is of interest to note, however, that dispersion data when some freezing was indicated were similar except for scale, i.e., the absolute values of dielectric constant and loss were smaller, but the frequency range and frequency dependence were insignificantly affected.

III. RESULTS

Equilibrium dielectric constant values measured in the range 1°C to -70°C are listed in Table I.

TABLE I

Equilibrium Dielectric Constants of Trimethylene Glycol

$T(^{\circ}K)$	274	262	247	234	224	215	209
ϵ_0	38.0	40.6	43.9	46.9	50.3	52.9	(54.0)*

*Evidence of slight solid formation.

Significant dispersion effects were measurable below -40°C in the available frequency range below 5 Mc/s, but only for temperatures of -58°, -64°, and -70 °C were measurements covering a substantial part of the dispersion region obtained.

The complex plane plots of real and imaginary parts, ϵ' and ϵ'', of the dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ in Figs. 2, 3, 4 show significant departures from the semi-circular locus predicted by the dispersion theories of Debye[2]
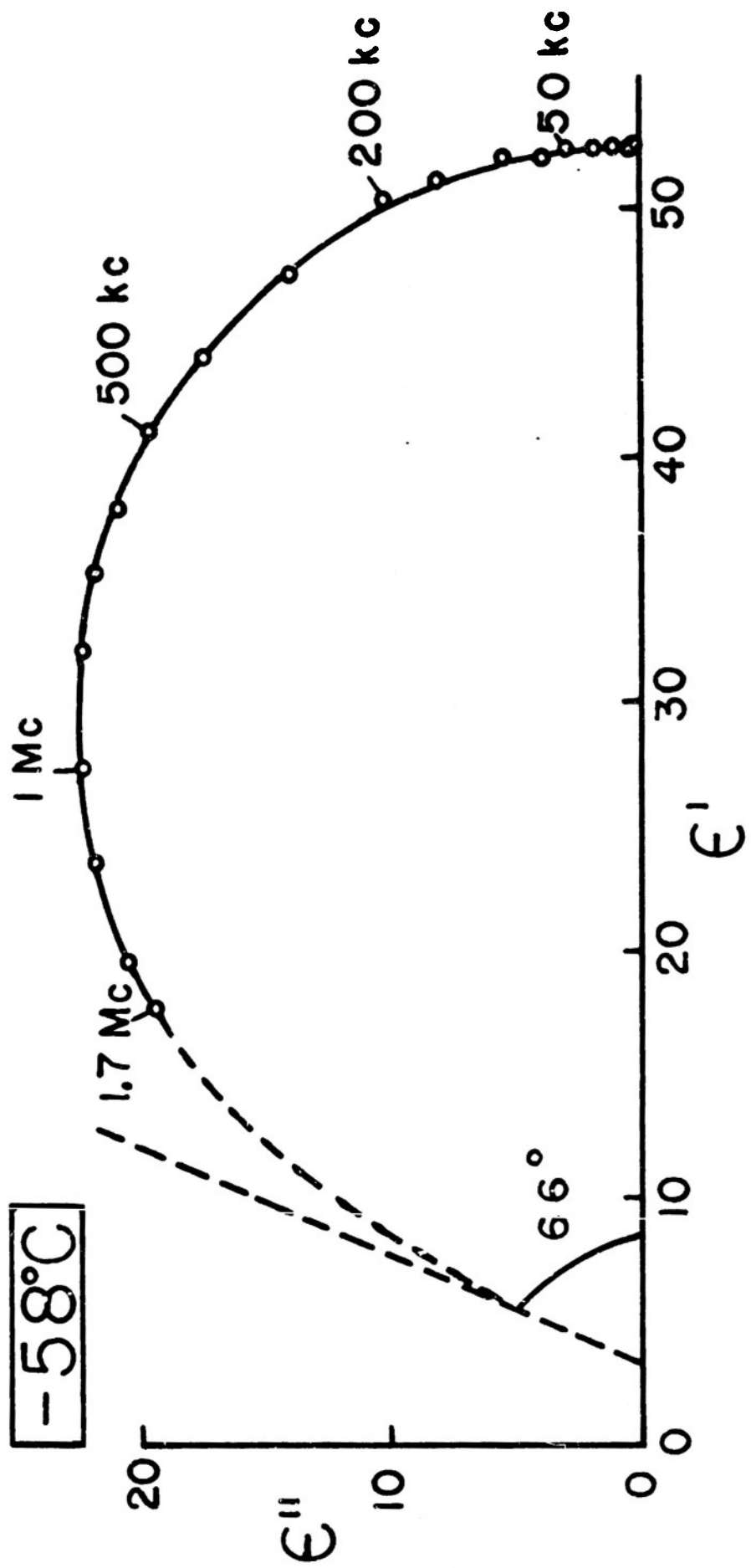
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2. P. Debye, Polar Molecules (Dover Publications, New York, 1929).
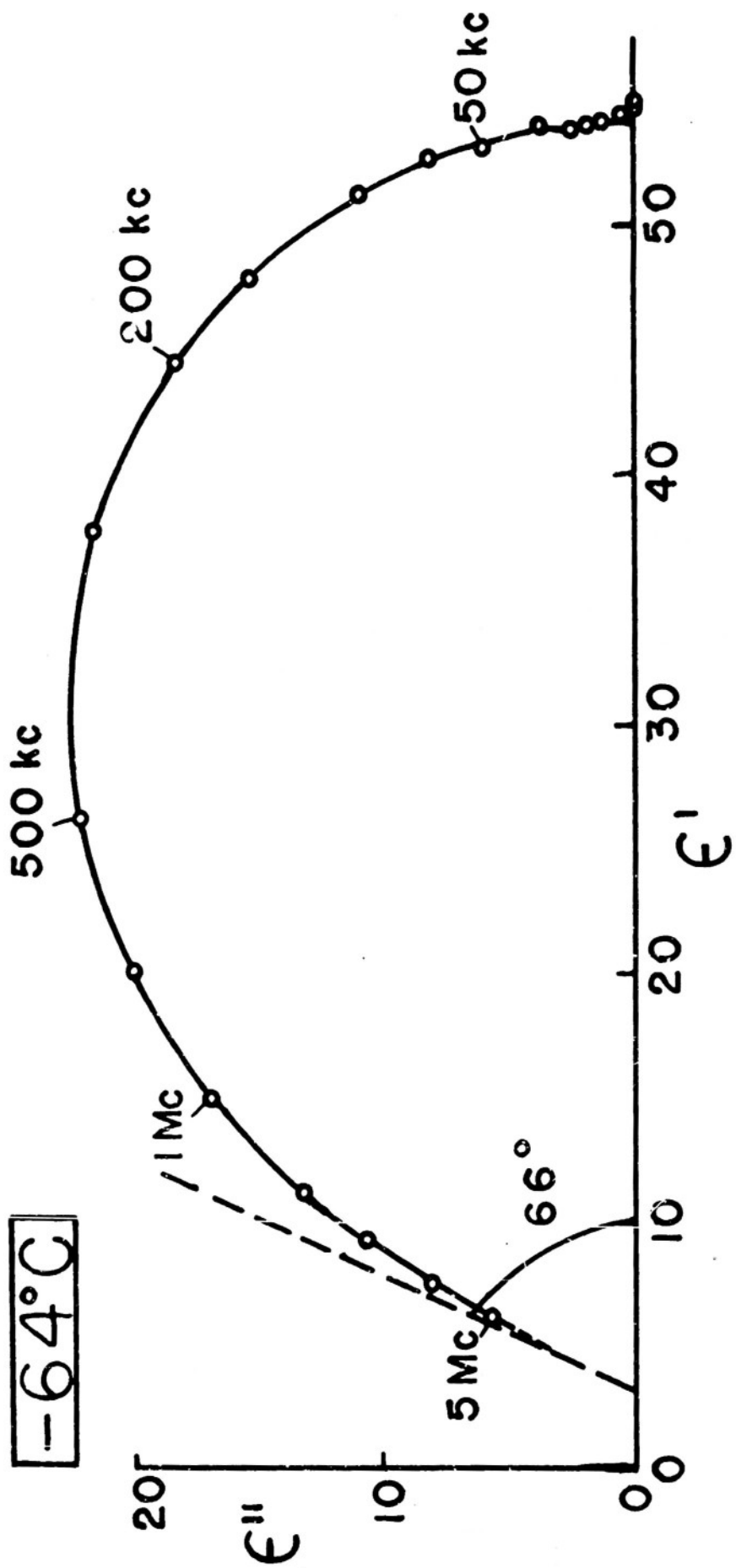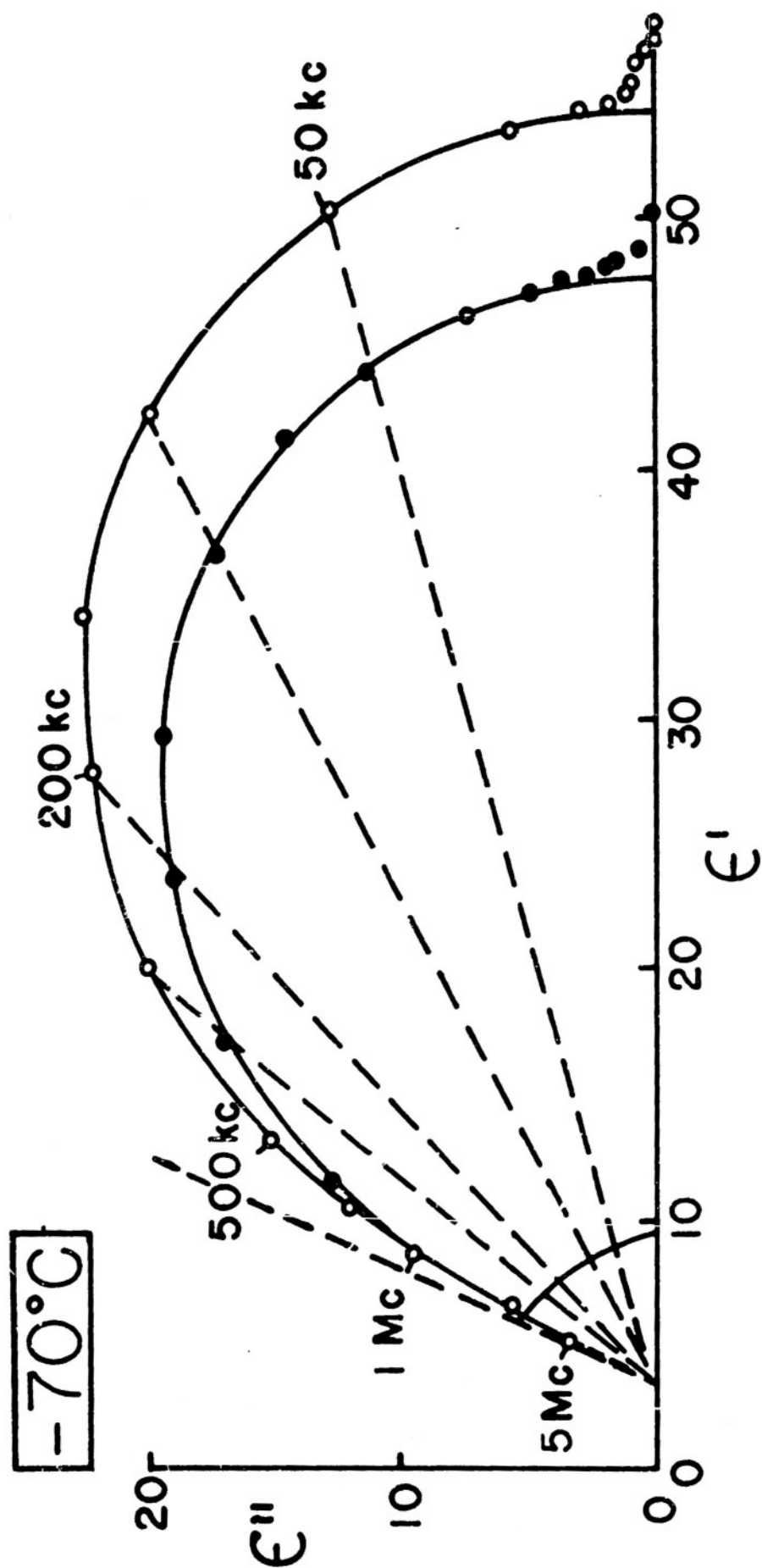---

Fig. 2.   Complex dielectric constant locus for trimethylene glycol at -58°C. Numbers by points are frequencies of measurements.

Fig. 3.   Complex dielectric constant locus for trimethylene glycol at -64°C.

Fig. 4.   Complex dielectric constant loci for two trimethylene glycol samples. Some freezing had occurred in both cases, to a larger extent in the sample giving the solid circles. The dashed straight lines connect points at the same frequencies and pass through the high frequency intercept at $\epsilon' \approx 3.5$.

and others[3]

3. See, for example, W. Kauzmann, Rev. Mod. Phys., 14, 12 (1942); J. H. Van Vleck and V. Weisskopf, Rev. Mod. Phys., 17, 227 (1945).

The data at -64°C in Fig. 3 define the dispersion quite completely with little possibility of significant solid formation. Within experimental error, the results are described by the empirical dispersion formula previously found to fit the data for propylene glycol and glycerol[1]:

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_1 + (\epsilon_o - \epsilon_1)/(1 + i\omega T)^\beta \qquad (1)$$

In this equation, ϵ_o and ϵ_1 are the limiting static and high frequency dielectric constants, $\omega = 2\pi$ frequency, T is a characteristic relaxation time, and β is an empirical parameter, $0 < \beta < 1$. The solid curves of Figs. 2, 3, 4 are drawn for $\beta = 0.74$ and are seen to be a good fit.

Both sets of data at -70°C plotted in Fig. 4 indicate some solid formation of perhaps 4 and 12 percent by volume (assuming spherical dispersed globules). It is significant that the two curves of ϵ'' versus ϵ' differ only in scale and not in frequency range, as shown by the fact that points at the same frequency lie on the dashed lines drawn from $\epsilon^* = \epsilon_1$. This agreement in frequency supports the conclusion that the frequency dependence and relaxation time T are not significantly affected by the solid particles formed at this temperature.

The data at -53°C are less complete and hence a less conclusive confirmation of Eq. (1) as a description of the dispersion process, but are consistent with what one would expect from the results at lower temperatures.

At temperatures above -58°C, only the beginnings of the

complete dispersion and loss region were reached at the highest frequency available (5 Mc/s). If the functional form of Eq. (1) is assumed to hold good, it is possible to deduce without serious error characteristic times $\mathcal{T}$ from the loss measurements below $-40°C$.

If Eq. (1) is expanded in powers of $\omega\mathcal{T}$, one obtains

$$\epsilon' = \epsilon_0 - (\epsilon_0 - \epsilon_1)\left[(\rho+1)(\omega\tau)^2 + O(\omega\tau)^4 + \dots \right],$$

$$\epsilon'' = (\epsilon_0 - \epsilon_1)\left[\rho(\omega\tau) - \rho(\rho+1)(\rho+2)(\omega\tau)^3 + O(\omega\tau)^5 + \dots \right]. \tag{2}$$

To a first approximation, the variation of ϵ' with frequency is a second order effect at low frequencies (i.e., as a constant minus a term quadratic in frequency), but the variation of ϵ'' is first order and linear in frequency. The latter is thus especially suitable and from Eq. (2) one has

$$\frac{\epsilon''}{f} \cong (\epsilon_0 - \epsilon_1)_{\rho} \cdot 2\pi\mathcal{T}_0. \tag{3}$$

Calculations of ϵ''/f from the measured conductance G^*

$^*G = 2\pi f C_g \epsilon''$, where C_g is the geometric cell capacitance.
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after correction for residual ohmic conductance gave essentially constant values except at frequencies so high that higher order terms in Eq. (2) are significant. Assuming $\rho = 0.74$ and $\epsilon_1 = 3.3$ as indicated by the lower temperature data permits calculation of or $f_1 = 1/(2\pi\mathcal{T})$ by use of Eq. (3). The values so obtained are listed in Table II, together with those from the more complete analyses possible for the data at $-58°$, $-64°$, and $-70°C$.

TABLE II

Relaxation Frequencies of Trimethylene Glycol

T(°K)	254	224	215	219	203
f_1(kc.'s)	4,850*	1,850*	614	315	130

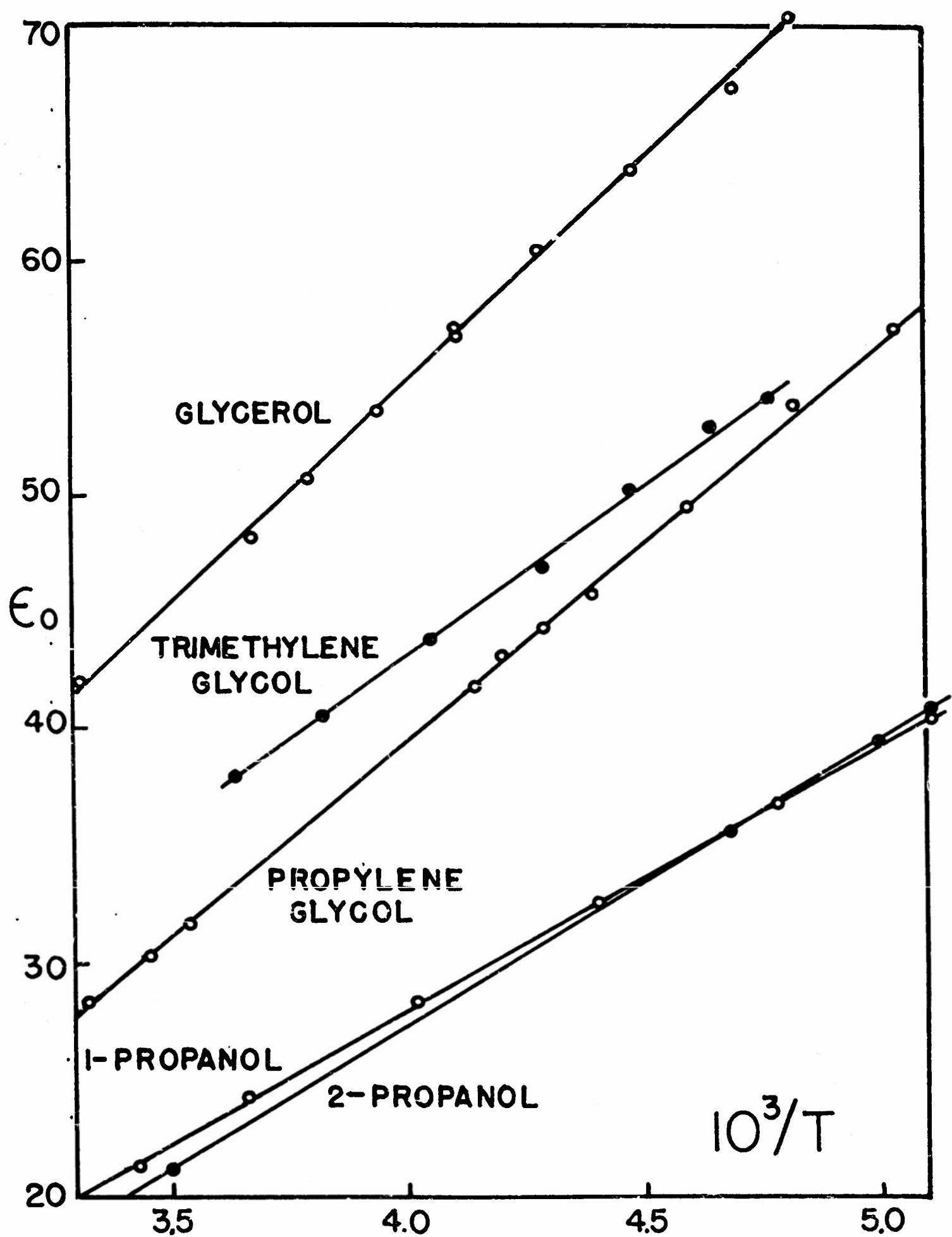*Inferred from variation of ϵ'' with f as discussed in text.

IV. DISCUSSION

The significant dielectric properties of trimethylene glycol obtained in this study are summarized by the values of the static dielectric constant ϵ_0, the limiting high frequency constant ϵ_1, the relaxation frequency f_1, and the empirical parameter β characterizing the frequency dependence of the dispersion. The values obtained are of most interest in comparison with those previously found for other three-carbon alcohols and glycols, in particular the isomer propylene glycol (1-2 propanediol) which has two adjacent hydroxyl groups rather than two on the end carbon atoms.

Dielectric constants ϵ_0 are plotted against reciprocal absolute temperature T in Fig. 5. The variations are approximately linear with 1/T as expected from theories of polar liquids, the values are roughly in proportion to the number of hydroxyl groups of the molecules, and isomeric effects are small but definite. In particular, the dielectric constants of trimethylene glycol are significantly larger than for propylene glycol, although the densities are practically the same (1.053 vs. 1.040 at room temperature), and it is reasonable to presume that a little more regular and effective coordination of neighbors by hydrogen bonding is possible for the former (evidence for such intermolecular bonding is discussed in Reference 1).

Fig. 5.   Static dielectric constants of three carbon
alcohols plotted against reciprocal absolute
temperature.

A

The limiting high frequency dielectric constants ϵ_1,
estimated by extrapolation in the present work, are not greatly
different for trimethylene and propylene glycol (3.3 and 3.5), nor
can any significant temperature dependence be deduced. The values
are significantly smaller than for 1-propanol (greater than 5.0)
and glycerol (approximately 4.2). No evidence was found in the
present measurements for the further dielectric relaxation process
or processes established to exist in 1-propanol and glycerol. The
available frequencies were too low to establish or deny such
dispersion in the present case, but its extent if present is
necessarily less.

The more striking differences among the various alcohols are
found in the parameters of the dispersion process.   The first
of these is the fact that the dispersion in trimethylene glycol
is considerably closer in form of its frequency dependence to
simple theory, but is definitely not in agreement.   This is
evident from the fact that the complex loci of Figs. 2, 3, 4 are
distinctly unsymmetrical and that the value of β for Eq. (1) to
fit the results is 0.74 rather than the value 1.0 for which Eq. (1)
reduces to the Debye equation.   The figure β = 0.74 is *thus*
significantly greater than β = 0.66 for the propylene glycol and
β = 0.60 for glycerol, and at the same time considerably smaller
than the value 1.0 of the Debye-like behavior of normal and iso-
propyl alcohols.

Although the nature of the approach to equilibrium is
evidently significantly affected by the presence of more than one
hydroxyl group on the molecule, it is also apparent that these
groups need not be on adjacent carbon atoms, and the results do

not lend themselves to an explanation wholly in terms of interaction of such neighboring groups.

The rates of approach to equilibrium with an applied field as characterized by the magnitude and temperature dependence of the relaxation frequency $f_0 (= 1/2\pi T)$ also are characteristically different for the various glycols. The rate plots in Fig. 6 of log f_1 versus $1/T$ show that the magnitude and slope for trimethylene glycol lie between those for 2-propanol and propylene glycol. Thus in the temperature range studied, the rate of orientation is an order of magnitude greater for the former and less for the latter. These differences could be attributed in part to progressively higher activation energies $\triangle H$ deduced from the slope of the rate plots of Fig. 6 and listed in Table III.
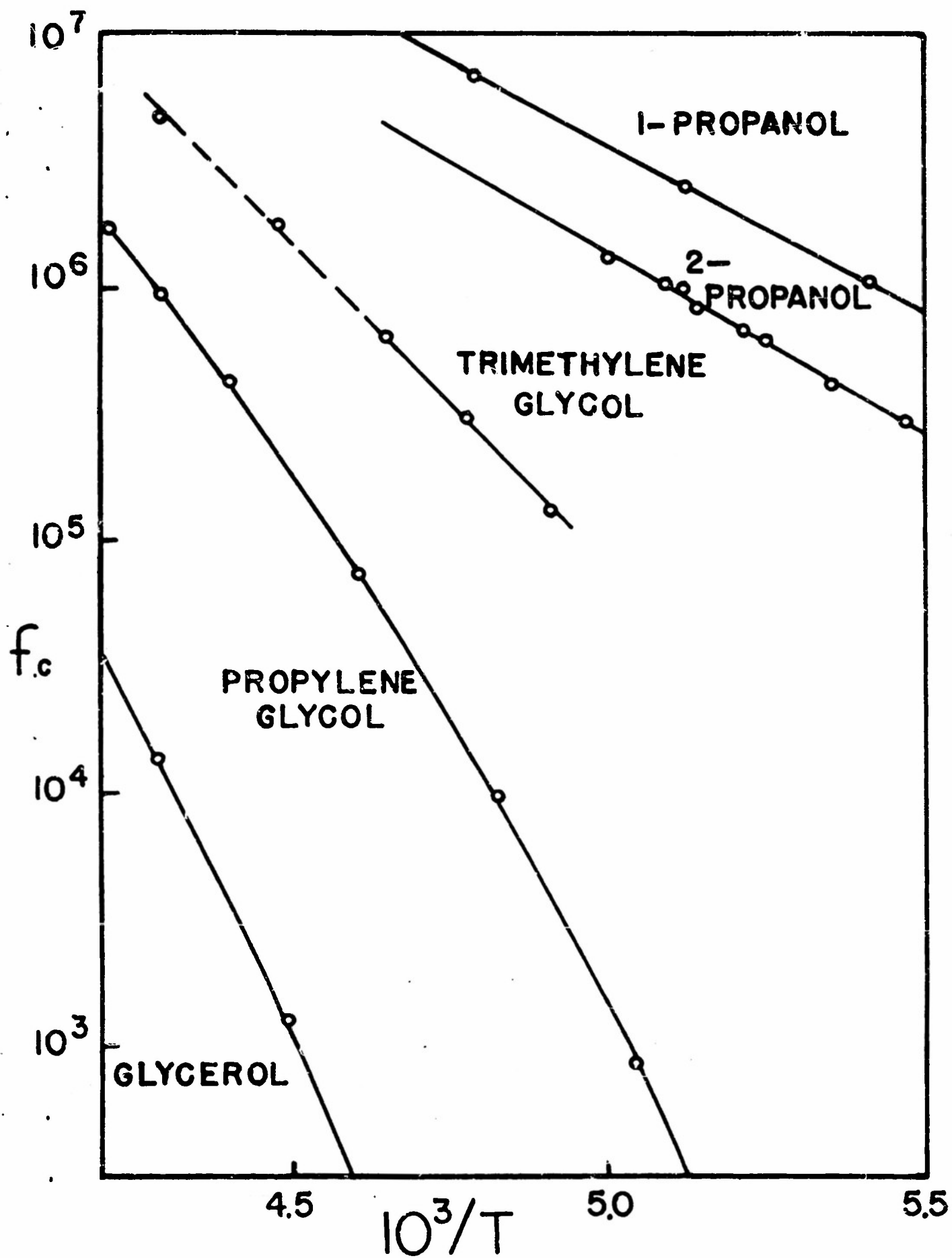
TABLE III

Apparent Activation Energies (kcal/mole) at 210°K

n-Propanol	iso-Propanol	Trimethylene Glycol	Propylene Glycol	Glycerol
5.0	5.9	12	19	32

The sequence is a not unreasonable one, as one would expect larger energy for reorientation of molecules with more polar groups, especially when in closer proximity. A detailed analysis of these activation energies in molecular terms is, however, unjustified, because the rate laws for all but trimethylene glycol have been found to deviate greatly from simple Arrhenius expressions ($f_1 = A\exp(-\triangle H/RT)$) where A and $\triangle H$ are temperature independent when sufficiently wide ranges of temperature are studied[1]. The nature of these deviations is shown by the portions of the propylene glycol data plotted in Fig. 6. The temperature range

Fig. 6. Relaxation frequencies f_c of principal dispersions of three carbon alcohols plotted against reciprocal absolute temperature.

of the data for trimethylene glycol is too limited to show the effect, but its absence would be surprising in view of the other evidence.

In summary, the differences between trimethylene and propylene glycol indicate a greater ease of orientation and more effective orientation for the former as well as smaller but still distinct deviations from the "ideal" frequency dependence of simple theory.   These differences and the deviations in opposite sense from the corresponding monohydroxy alcohols are all qualitatively reasonable for a molecule containing two non-adjacent hydroxyl groups.

It seems clear that a fundamental explanation must be in terms of intermolecular forces, hydrogen bonding especially, and steric constraints imposed by the molecular structure. Although further study of related systems may aid significantly in formulation of adequate theory, the available measurements at present provide quite comprehensive and specific results by which such theory may be tested.

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